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FROST RESISTANCE OF CONCRETE WITH HIGH CONTENTS OF FLY ASH - A STUDY ON HOW HOLLOW FLY ASH PARTICLES DISTORT THE AIR VOID ANALYSIS

Marianne Tange Hasholt, Katja Udbye Christensen, and Claus Pade

Abstract

Cenospheres are hollow fly ash particles. When performing air void analysis on a contrast enhanced plane section, air inclusions in cenospheres are counted as air voids. In the present study, air void analyses for air entrained concrete mixtures with fly ash (up to 50% of binder mass) were corrected based on chord counting for non-air entrained paste samples with various contents of fly ash. The correction only lead to a small reduction of the total air content, but it increased the spacing factor up to 25%. The concrete mixtures were also exposed to salt frost scaling testing. The amounts of scaling were unacceptable for several mixtures with high dosages of fly ash. Inferior strength or inadequate air void structure could not explain this. Additional testing pointed to that chemical surface degradation aggravated the physical frost attack for concrete mixtures with high contents of fly ash.

1. Introduction

Fly ash has been used in concrete production for many years [1]. There are economic, environmental as well as technological reasons to substitute part of the cement with fly ash. For example, fly ash addition reduces heat development at early age [2], and there is evidence that fly ash addition can reduce chloride ingress, thereby making reinforced concrete structures more durable [3].

Typically, the fly ash dosage in structural concrete is moderate, i.e. 15-25% of the binder content [1]. However, recent years increasing awareness of the environmental impact of concrete production has promoted a demand for concrete with higher fly ash dosages, as increased fly ash addition is one way to lower the cement content and thereby the carbon footprint of concrete.

Salt frost scaling resistance seems to be a weak point for concrete produced with high volumes of fly ash, where fly ash constitutes e.g. 50% of the binder. There are many studies documenting that the salt frost scaling resistance of concrete with cement as the only powder is superior to the salt frost scaling resistance of concrete with fly ash. However, in many of the studies, it can be argued that concrete with and without fly ash are not compared on an equal footing:

- The concrete mixtures have the same water/binder ratio (W/B), i.e. fly ash replaces cement on a 1:1 mass basis. This procedure results in fly ash mixtures with lower strength than the reference mixtures based on pure cement [4].
- The concrete mixtures are air entrained, and the dosage of air-entraining admixture (AEA) is adjusted to obtain approximately the same air content in the fresh concrete [4, 5]. Fly ash normally contains small amounts of unburnt carbon that can adsorb the AEA, making it inactive [6]. Therefore, concrete with fly ash typically needs a higher dosage of AEA than concrete without fly ash to obtain the same amount of air in the fresh concrete. However, as shown by Siebel [7], comparable total air contents is not a sufficient precondition for having comparable air void structures. If the concrete mixtures also include (super)plasticizers in varying dosages, concrete mixtures with identical air contents may have very different air void structures in terms of specific surface of the air voids and spacing factor. Many of the studies on the effect of fly ash addition on salt frost scaling do not include air void analysis of the hardened concrete, so it

is not possible to judge if the air void structures of the concrete mixtures will provide comparable protection against frost attack.

- The concrete mixtures have the same age at the initiation of the salt frost scaling test. The pozzolan reaction, where fly ash reacts to form gel solid, is much slower than the hydration of cement. Most standardized salt frost scaling tests are initiated 14 or 28 days after casting, and this is not enough for concrete with fly ash to reach its full potential as regards frost resistance. The problem becomes larger, when the fly ash dosage increases. Both [8] and [9] show that the salt frost scaling of concrete with high volumes of fly ash is reduced significantly, if the start of the freeze/thaw exposure is postponed to 91 or 180 days after casting.
- The same curing procedure is used prior to the frost test, no matter if the concrete mixture composition includes fly ash or not. The curing procedure after demoulding normally consists of a moist curing period (in water bath or fog room) and a drying period, where the concrete is stored exposed to air with RH significantly lower than 100%, e.g. 50% or 65%. Ehrhardt [10] showed that if using a relatively rapid hardening binder combination (2 days strength > 23 MPa, where cement strength is measured according to EN 196-1), adequate salt frost scaling resistance was obtained with a short moist curing period or even no moist curing at all. Slower reacting binder combinations experienced harmful drying, resulting in poor surface quality, and for this reason the concrete surface could not sustain a salt frost scaling test.

There are also studies showing that concrete with high volumes of fly ash, i.e. where fly ash constitutes 50% or more of the binder, can possess adequate salt frost scaling resistance [11]. Concrete with high volumes of fly ash may be more sensitive to finishing and curing conditions, but if the concrete work is carried out correctly, concrete with high volumes of fly ash has shown excellent salt frost scaling resistance for e.g. pavements in service. For this reason, current best

practice for high-volume fly ash concrete do not advice against using the concrete in environments where it is going to be exposed to frost and de-icing chemicals [12].

In a Danish development project “Green Transition of Cement and Concrete Production” aiming at improving the environmental profile of concrete production, various properties were tested for concrete, where fly ash made up 40-50% of the binder mass. Despite several attempts, none of the mixtures passed an accelerated salt frost scaling test. The above-mentioned reasons for poor salt frost scaling resistance could be discarded. The concrete mixtures with high contents of fly ash were designed to have 28 days compressive strength comparable to a frost resistant reference mixture, which had a much lower fly ash content. Therefore, the W/B was not fixed; the slower property development of mixtures with high fly ash contents were compensated by lowering the W/B. The dosage of AEA was also variable. Air void analysis of the hardened concrete showed that concrete with high contents of fly ash fulfilled all requirements to frost resistant concrete, and e.g. the spacing factor was on the same level as for the reference concrete. Last, the accelerated salt frost scaling test was carried out on saw cut surfaces, so e.g. poor concrete surface quality would not influence the result.

It was speculated that hollow fly ash particles would be counted as air voids in the air void analysis without contributing to the frost resistance as entrained air voids, thereby making the outcome of the air void analysis for concrete with high contents of fly ash misleading. Fly ash is a by-product from coal combustion. At high temperatures, carbon and volatile matter burn, whereas mineral impurities in the coal melt and form droplets. Fly ash particles are the cooled droplets, and they are therefore spherical. Most of the fly ash particles are solid, but a small percentage is hollow particles

called cenospheres. The presence of cenospheres can easily be observed by suspending the fly ash particles in water, see figure 1:

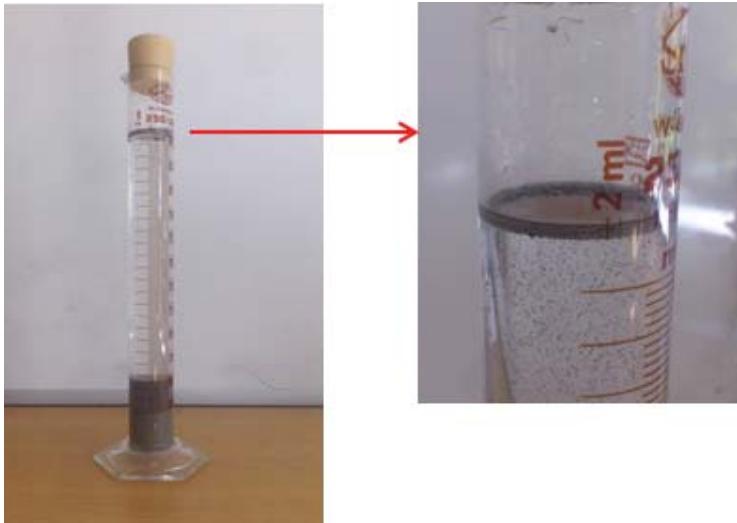


Figure 1: When fly ash is suspended in water, the solid particles will settle at the bottom (left), while the much lighter cenospheres gather at the water surface.

In an air void analysis based on black and white color impregnation of a plane section, the empty cavities of cenospheres will look like air voids. The error in the air void analysis is larger, the larger the fly ash content. It was therefore decided to investigate if the presence of cenospheres could have a significant effect on the outcome of the air void analysis. The investigation was carried out as part of a Master thesis work at the Technical University of Denmark [13].

2. Materials and methods

2.1 Reference concrete

In Denmark, concrete requirements are a combination of prescriptive requirements and performance-based requirements. According to DS 2426 [14] and the Danish Road Directorate's standard specification for bridges, concrete exposed to severe freeze/thaw exposure (exposure class XF4 according to EN 206 [15]) has to fulfill the following:

- Cement type: CEM I; minimum strength class: 42.5; sulfate resistance class: SR5 or better
- Maximum fly ash content: $FA/C = 0.33$ (i.e. $FA/(C+FA) = 0.25$)
- Maximum W/C_{eq} : 0.40 (according to DS 2426, fly ash content up to 33% of the cement content can be taken into account by using an activity factor ($W/C_{eq} = W/(C+0.5 \cdot FA)$))
- Minimum strength class: C40/50
- Minimum air content in fresh concrete: 4.5%
- Frost resistance: The concrete has either passed an accelerated freeze/thaw test, or an air void analysis of the hardened concrete has documented
 - air content in hardened concrete: 3.5% or higher
 - spacing factor in hardened concrete: 0.20 mm or lower

Concrete mixtures with high contents of fly ash ($FA/(C+FA) > 0.25$) cannot fulfill the prescriptive requirement regarding maximum fly ash content. Typically, concrete mixtures with high contents of fly ash are also challenged as regards maximum W/C_{eq} , as only a part of the fly ash is taken into consideration when calculating the W/C_{eq} . This was one of the issues that initiated the development project "Green transition of cement and concrete production". In this project, one of the goals is to

work towards purely performance-based specifications, as the prescriptive requirements often become an obstacle for implementing more environmentally friendly solutions.

In the present project, the reference concrete (starting point for development of concrete mixtures) was a concrete mixture from a ready mix plant that fulfilled all the above-mentioned prescriptive requirements:

- Cement type: CEM I 42.5 N – SR5 (alkali content < 0.4%)
- $FA/(C+FA) = 0.13$
- $W/C_{eq} = 0.37$

The aim was to obtain comparable technical performance with regard to workability, compressive strength, and salt frost scaling resistance (see section 2.3 for exact requirements). The carbon footprint of the cement used in the reference concrete was relatively high. Therefore, it was decided to use another type of cement (CEM I 52.5 N) with a lower carbon footprint. Because of the higher strength potential of the cement, the W/C_{eq} was increased to obtain the same compressive strength as the reference concrete. Therefore, none of the mixtures in the present study met the Danish rules as regards maximum W/C_{eq} .

2.2 Materials

The cement used in the study was type CEM I 52.5 N according to EN 197-1 [16]. The fly ash used was low in calcium oxide (CaO) and conformed to EN 450-1 [17]. The chemical compositions of cement and fly ash are shown in table 1. Chemical analyses have not been performed as part of this

project, so chemical compositions are according to information from the manufacturers. For the fly ash, it is an average for 6 months of production.

Table 1: Chemical composition of powders. Figures are in unit [% of powder mass].

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	Na ₂ O eq	Cl ⁻	LOI
Cement	64.5	19.7	5.2	3.8	3.3	0.6	≤ 0.05	1.7
Fly ash	3.9	56.4	21.6	5.4	0.6	2.9	≤ 0.05	2.1

Tap water was used as mixing water.

The coarse aggregates were 3 size fractions of crushed granite. They were all suitable for aggressive environment (frost and chloride exposure, exposure classes XF4 according to EN 206 [15]).

Two chemical additives were used:

- superplasticizer, active component: polycarboxylates
- air entraining agent, active component: tensides

2.3 Concrete specimens

Concrete compositions for mixtures with various contents of fly ash were developed in a 3 step process. The process followed the same procedure as the Danish development project “Green Transition of Cement and Concrete Production” (mentioned in section 1), where concrete mixtures with high contents of fly ash had failed accelerated salt frost scaling testing.

First, a desktop calculation was made, based on a performance-based design procedure developed in the project “Green Transition of Cement and Concrete Production”. The design procedure is described in [18]. The procedure is based on interpolation between results obtained for concrete mixtures with varying fly ash contents. The design procedure ensures that the concrete mixture with the highest cement substitution that fulfills the technical requirements will be chosen, thereby leading to a concrete composition with minimum carbon footprint. Concrete compositions were developed with FA/(C+FA) 0%, 25%, 33%, 44%, and 50%, aiming at the same workability, air content, and compressive strength for all mixtures:

- Slump: 125 mm
- Air content in fresh concrete: 6%
- Compressive strength after 28 days of curing at 20°C: 42 MPa

The aggregate content and combination was identical in all mixtures, i.e. changes only concerned the composition of the paste. Mixtures were identified by their FA/(C+FA) ratio. For example, mixture 033 is the mixture with $FA/(C+FA) = 33\%$.

Second, trial mixing was performed for all concrete compositions. Trial mixing was performed by mixing 9 l concrete in a small laboratory pan mixer. Here, the slump and air content of the fresh concrete were measured. The following acceptance criteria were used:

- Slump: 125 ± 25 mm
- Air content in fresh concrete: $6.0 \pm 1.0\%$

199 If the fresh concrete properties did not match the acceptance criteria, the dosages of superplasticizer
200 and air entraining agent were adjusted, until the fresh concrete properties were satisfactory. From
201 the last trial mix of all concrete compositions, specimens were cast for measurements of
202 compressive strength, before the compositions were finally approved.

203
204 The final concrete compositions are shown in table 2. When reviewing the compositions for
205 mixtures 000-050, it was noticed that the dosage of superplasticizer increased, when the content of
206 fly ash increased. It was expected that the dosage of air entraining agent would also unequivocally
207 increase, when the fly ash content increased. However, the figures showed that the amount of air
208 entraining agent reached a maximum at $FA/(C+FA) = 0.25$. Superplasticizers sometimes also
209 possess air entraining abilities, and then to keep a constant total air content, it is necessary to reduce
210 the dosage of air entraining agent. However, air voids generated by a superplasticizer typically are
211 coarser than air voids generated by an air entraining agent [7]. It was therefore decided to add an
212 extra mixture to the experimental program. This mixture should represent the combination of a high
213 $FA/(C+FA)$ and a high dosage of air entraining agent. This mixture was called 050EA (EA: Extra
214 Air entraining admixture). 050EA was identical to mixture 050, except for the AEA dosage, which
215 was identical to mixture 025 that had the highest dosage of AEA of all the other mixtures. This
216 dosage also corresponded to the maximum recommended dosage according to the technical data
217 sheet from the AEA manufacturer. During the trial mixing of mixture 050EA, the dosage of AEA
218 was not adjusted to meet target values of fresh concrete properties. A small adjustment was made
219 for the dosage of superplasticizer to meet the target slump. The mixture was approved after it was
220 ensured that the mixture did not show signs of separation or other aspects that could cause casting
221 difficulties. Compressive strength was not used as acceptance criterion for mixture 050EA, as it was
222 expected that the high air content registered in the fresh concrete would lead to a strength reduction.

223

224 *Table 2: Concrete compositions (expected air content in fresh concrete: 6%). Aggregates are in*
 225 *saturated, surface dry condition.*

Constituents	Density	Mixture					
		000	025	033	044	050	050EA
	[kg/m ³]	[kg/m ³]	[kg/m ³]	[kg/m ³]	[kg/m ³]	[kg/m ³]	[kg/m ³]
Cement	3160	372	291	267	234	218	218
Fly ash	2300	-	96	133	188	218	218
Water	1000	181	170	156	144	135	131
Sand, 0-4 mm	2620	620					
Coarse agg., 5-8 mm	2700	173					
Coarse agg., 8-16 mm	2720	370					
Coarse agg., 16-25 mm	2720	544					
Superplasticizer	1050	0.2	0.4	0.8	1.9	2.6	2.8
Air entraining agent	1010	4.5	7.0	5.0	2.5	2.7	7.0

226

227 Third, all mixtures were prepared in a pan mixer of semi-industrial size (batch size 175 l). Previous
 228 experience had shown good reproducibility between results obtained using the laboratory mixer
 229 used for trial mixing and the larger mixer. For each mixture, slump and air content in fresh concrete
 230 were measured according to Euro norms [19, 20]. If the measurements corresponded to expected
 231 values (i.e. values from the trial casting) within reasonable accuracy, the mixture was used to cast
 232 18 Ø150 x 300 mm cylinders. The specimens were de-moulded 24 h after casting. The subsequent
 233 curing of the test specimens depended on the test method that the specimens were going to be used
 234 for, i.e. testing of compressive strength (section 2.5), air void analysis (section 2.6) and accelerated
 235 salt frost scaling testing (section 2.7).

236

237 **2.4 Paste specimens**

238 Paste samples were produced to investigate how the presence of fly ash cenospheres can influence
239 the outcome of air void analysis of hardened concrete. Each paste mixture corresponded to a
240 concrete mixture, see table 2. The paste was produced using cement, possibly fly ash, and water.
241 The paste was prepared without superplasticizer and air entraining agent, so the paste was not in
242 any way air entrained. It was assumed that air voids registered during the air void analysis would
243 mainly be due to cenospheres.

244

245 0.4 l paste was produced for each mixture. The paste was mixed manually. The mixing water was
246 gradually added to the powder to ensure a homogenous paste without lumps. When all water had
247 been added, the paste was mixed for 3 minutes. The paste was cast in Ø22 x 120 mm cylindrical
248 tubes (1 tube per mixture). The paste was cautiously placed in the tubes to prevent entrapped air.
249 During the first 24 hours of hardening, the tubes were rotated to prevent separation. After 24 hours,
250 the tubes were de-moulded and the paste specimens were sealed and stored in a climate room
251 (20°C) until time of air void analysis.

252

253 **2.5 Compressive strength**

254 The compressive strength was measured according to EN 12390-3 [21]. The test was carried out for
255 3 specimens from each mixture. After de-moulding, the specimens were placed in a 20°C water
256 bath, and the test was carried out, when the test specimens were 28 days old. It was decided to
257 strictly follow the standardized test, including the before-mentioned curing regime, even though this
258 meant that the curing conditions for specimens for compressive strength testing and for accelerated
259 salt frost scaling testing were not alike, see section 2.7.

2.6 Air void analysis of hardened paste and concrete samples

The air void analyses were carried out according to EN 480-11 [22], using the RapidAir image analysis system for measurements of the air void parameters.

Air void analyses were carried out for 2 concrete cylinders for each mixture (total traverse length: 1200 mm per specimen). After de-moulding, the cylinders were stored in water (20°C) until the time of testing. All concrete specimens were at least 14 days old at time of testing. The air void structure does not change in the hardened concrete. Therefore, time of testing is not critical, as long as the concrete strength is adequate to ensure good sample preparation.

The air void analysis was carried out for one paste cylinder for each mixture (at least 14 days at time of testing). The specimen was saw cut both crosswise and lengthwise and then glued together, see figure 2. This was done to obtain a test area that at the same time was as large as possible, and almost quadratic, as this eased the grinding. By doing so, the test area became approx. 60 mm x 95 mm. The total traverse length for each specimen was 600 mm. This was only half of the required traverse length according to [22]. However, the purpose of this standard is to analyze concrete and mortar, not paste. For concrete samples, aggregates normally constitute more than 50% of the test area, and the traverse length in paste is therefore less than 600 mm. Thus, the traverse length for the paste samples in the present study was longer than the traverse length in paste for concrete samples. For this reason, it was considered acceptable to reduce the traverse length to 600 mm.

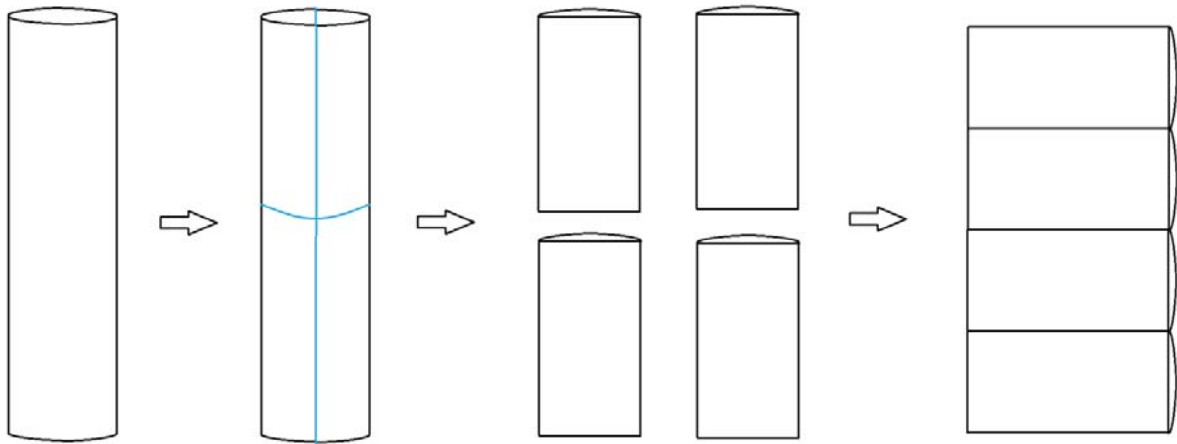


Figure 2: Cutting and gluing of paste specimens for air void analysis.

2.7 Accelerated salt frost scaling test

Accelerated salt frost scaling tests were carried out according to the reference method in CEN/TS 12390-9 [23]. After de-moulding, concrete cylinders were stored 6 days in water (20°C), and then stored in climate chamber (20°C, 65% RH) until the age of 28 days. During the period in climate chamber, the specimens were only removed for short periods of time to saw cut the specimens (day 21) and to glue on a rubber sleeve (day 25). The rubber sleeve made it possible to establish a liquid reservoir on top of the specimen. At the age of 28 days, the test surface was covered with 3 mm of de-ionised water to obtain capillary saturation in the surface layer. The specimen was covered with a plastic sheet to prevent evaporation. At the age of 31 days, the de-ionised water was replaced with a 3% NaCl solution, and the freeze-thaw exposure was initiated by placing the specimens in a freezing chamber. The freezing chamber was controlled by a thermocouple placed in the liquid layer on one of the test specimens. The temperature in the liquid layer followed a temperature cycle defined in the standard. During the temperature cycle, the temperature started at +20°C and was then gradually decreased to -20°C, before the temperature was again increased to +20°C. Each

temperature cycle lasted 24 h, and the samples were exposed to a total of 56 cycles. Scaled material from the samples were collected after 7, 14, 28, 42, and 56 cycles.

3. Results and discussion

3.1 Results from concrete samples

The results from testing performed on the concrete specimens are shown in table 3. Where nothing else is mentioned, the results are for concrete from the final mixtures. However, as regards compressive strength, results are shown both for concrete from the trial mixtures and the final mixtures (concrete compositions are identical).

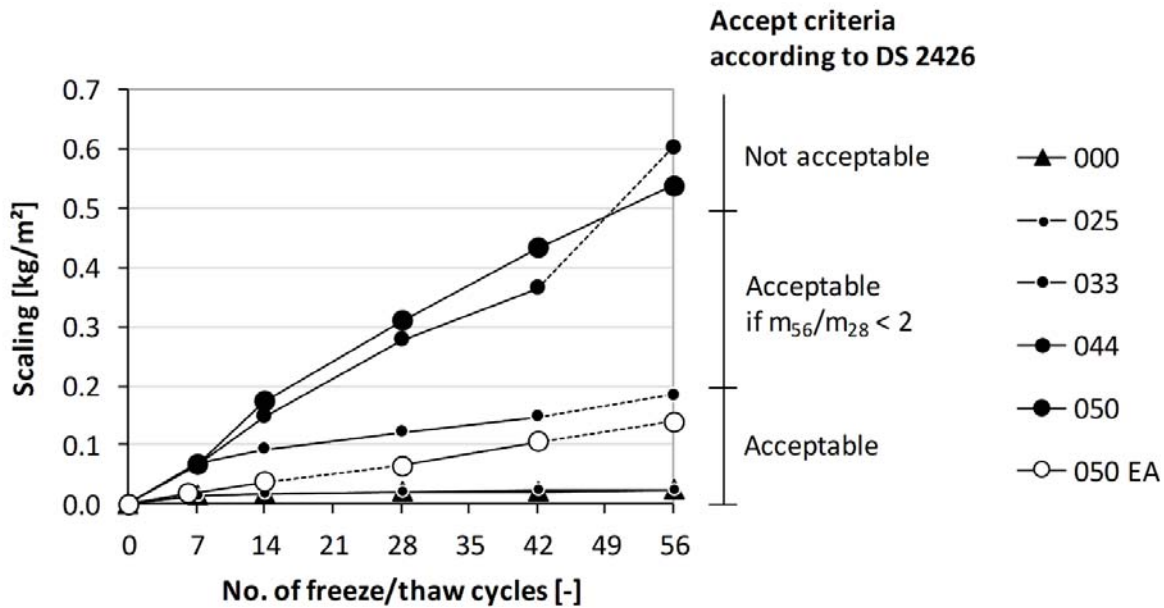
310 Table 3: Results from tests performed on fresh and hardened concrete.

Mixture ID	Slump	Air content in fresh concrete	Air content in hardened concrete	Specific surface	Spacing factor	Compressive strength trial mix	Compressive strength final mix	Accumulated scaling after 28 cycles	Accumulated scaling after 56 cycles
	[mm]	A _{fresh} [%]	A _{hard} [%]	S [mm ⁻¹]	L [mm]	[MPa]	[MPa]	m ₂₈ [kg]	m ₂₈ [kg]
000	110	6.4	7.33	42.2	0.081	42.9	44.1	0.02	0.02
025	110	7.0	6.44	47.1	0.080	39.2	38.8	0.02	0.03
033	110	5.6	5.03	40.8	0.118	-(1)	46.2	0.12	0.19
044	125	5.8	4.31	44.2	0.112	41.7	59.5	0.28	0.60
050	125	5.5	4.74	40.4	0.119	44.4	61.3	0.31	0.54
050EA	100	8.5	7.57	44.3	0.075	-(2)	40.9	0.07	0.14

- 311 1. The compressive strength for mixture 033 was not measured for specimens from the trial casting
312 (unintentional omission).
313 2. The compressive strength for mixture 050EA was not measured during trial casting. Due to the
314 increased dosage of air entraining agent compared to mixture 050, mixture 050EA was expected
315 to have lower strength than mixture 000, and therefore equal strength was not an accept criterion
316 for mixture 050EA during trial casting.
317

318 The development in salt frost scaling is shown in figure 3. Unfortunately, the freezing chamber
319 broke down twice during the test period. This happened during a weekend and during a public
320 holiday, so each time the problem was unfortunately not discovered before several days later.
321 During the break downs, the freezing chamber did not start a new freeze/thaw cycle, and the
322 specimens were stored at approx. 25°C. When the problem was discovered, the freezing chamber
323 was restarted, and the test period was prolonged, so all specimens experienced 56 freeze/thaw
324 cycles. As the mixtures had not been cast on the same day, the specimens did not have the same
325 age, when the problem with the freezing chamber occurred. The dashed line between two markers
326 indicate for each mixture when the problem occurred.

327



328

329 *Figure 3: Development of freeze/thaw scaling in the experiment together with acceptance criteria*
 330 *for cumulated scaling after 56 freeze/thaw cycles according to DS 2426 [14] (DS 2426 allows more*
 331 *scaling, if the development of scaling is not accelerating, i.e. $m_{56}/m_{28} < 2$).*

332

333 Based on results shown in table 4 and in figure 3, the following is observed:

334

- 335 • The properties of the fresh concrete, i.e. slump and air content, are as expected.
- 336 • If not taking mixture 050EA into account, there seems to be a trend, where the total air content
 337 in the hardened concrete is reduced, when the fly ash content is increased. This may be because
 338 the dosage of AEA is low in the mixtures with high contents of fly ash, i.e. the dosage of AEA
 339 is lower in mixture 044 and 050 than in mixture 000, and this may cause the air voids to be less
 340 stable in mixtures with high fly ash contents.

- Even though the total air content of mixtures with high volumes of fly ash are reduced, they still show low spacing factors. The largest spacing factor is registered for mixture 050, and here the value is 0.119 mm. This is well below 0.20 mm, which is often considered the critical spacing factor [24].
- For the trial mixtures, the 28 days compressive strength is on the same level for all mixtures (39.2-44.4 MPa).
- For the final mixtures, mixtures 000, 025, and 033 show compressive strength on the same level as the trial mixtures. For mixtures 044 and 050, the compressive strengths are much higher than for the corresponding trial mixtures; the compressive strength of mixtures 044 and 050 are 59.5 MPa and 61.3 MPa, respectively, compared to 44.1 MPa for mixture 000. The reason why the compressive strengths of mixtures 044 and 050 are higher is not known. The compressive strength of mixture 050EA is 8% lower than for mixture 000. This may be due to the high total air content of mixture 050EA; it shows the highest air content of all mixtures, both in the fresh and in the hardened concrete.
- None of the mixtures showed accelerating scaling during the 56 freeze/thaw cycles, i.e. in all cases the cumulated scaling after 56 cycles m_{56} is less than twice the amount of cumulated scaling after 28 cycles m_{28} ($m_{56}/m_{28} < 2$). DS 2426 sets up different acceptance criteria depending on if the scaling is accelerating or not. In the present case, where the development of scaling is not accelerating, up to 0.50 kg/m² scaling after 56 freeze/thaw cycles is acceptable.
- The frost resistance of mixtures 044 and 050 were not acceptable, even though they showed high compressive strength and acceptable air void structures.
- Mixture 050EA showed acceptable frost resistance. However, even though mixture 050EA both had the highest total air content and the lowest spacing factor of all mixtures, the frost resistance of mixture 050EA was not as good as the frost resistance of mixtures 000 and 025.

3.2 Results from paste samples

Table 4 shows the results from the air void analysis of paste samples:

Table 4: Air void analysis of hardened paste samples.

Mixture ID	Air content in hardened paste	Specific surface	Spacing factor
	A_{hard} [%]	S [mm ⁻¹]	L [mm]
000	0.75	30.3	0.611
025	1.75	63.0	0.212
033	1.26	88.6	0.171
044	2.63	57.2	0.197
050	2.10	98.4	0.125

The general trend is that the total air content as well as the specific surface of air voids registered in the hardened paste sample increase, when the fly ash content increases. As a consequence, the spacing factor decreases, when the fly ash content increases. None of the samples are air entrained, so they should show spacing factors considerably higher than the critical spacing factor of 0.20 mm. This is also the case for the reference mixture (mixture 000), but the mixtures with the highest fly ash contents, i.e. mixtures 033, 044, and 050, all show spacing factors lower than 0.20 mm.

In the paste mixtures 000, 025, 033, 044, and 050, the fly ash makes up 0%, 14%, 19%, 27%, and 32% of the paste volume. If the cenospheres show up as air voids in the air void analysis, then the number of chords in each size interval is proportional to the fly ash volume. Therefore, the number

of chords in each of the 28 chord size intervals according to EN 480-11 is plotted as a function of volumetric fly ash content. Figure 4 shows the plots for 3 different chord size intervals:

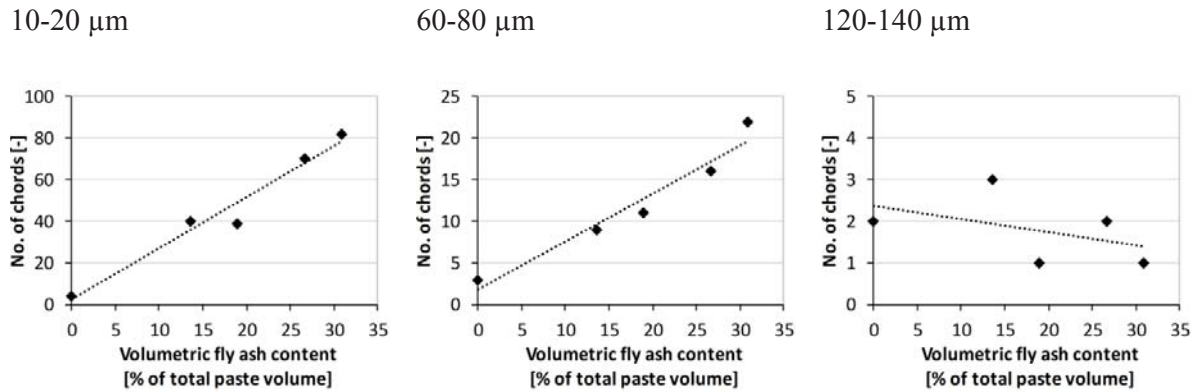
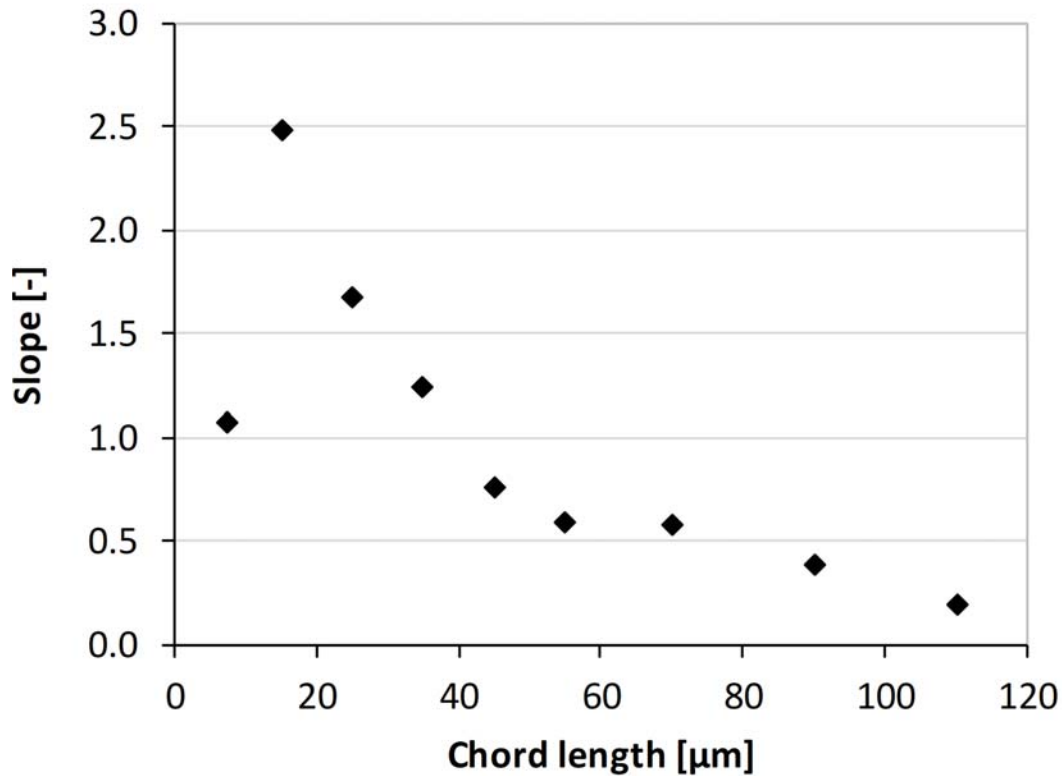


Figure 4: Number of chords versus volumetric fly ash content, plotted for 3 different chord size intervals (Note: Scaling of vertical axes are different).

Up to chord size interval 100-120 μm , there is a linear relation between the number of registered chords in the size interval and the fly ash volume. When there is no fly ash in the cement paste, nearly no chords are registered, and then the number of chords increases, when the fly ash volume increases. From chord size 120-140 μm and up, the number of registered chords are in all cases low, and their number seems to be at random with no relation to fly ash content. This supports the hypothesis that the presence of cenospheres distort the outcome of the air void analysis. At small chord sizes, many of the registered voids are not air voids but cenospheres. For the majority of the fly ash particles, the diameter is less than 100 μm , and therefore the cenospheres do not add to the registered number of chords at larger chord sizes. Here, it is entrapped air that is registered. Even though the paste samples were carefully compacted, the entrapped air could not be completely avoided, but the amount of entrapped air does not seem to be correlated to the fly ash content.

399 From the slope of the trend line in each graph up to chord size 100-120 μm , it is possible to
400 calculate how much the presence of cenospheres contribute to the air void analysis, see figure 5:
401



402 *Figure 5: The contribution of cenospheres to the air void analysis. The slope has been determined*
403 *for separate graphs like those shown in figure 4. The slope corresponds to the number of chords per*
404 *600 mm traverse length, when the volumetric fly ash content is 1% of the paste volume.*

405

406 Figure 5 shows that except for the smallest chord size interval (0-10 μm), the graph is a gradually
407 decreasing line. The reason for the low number of chords in the size interval 0-10 μm is that the
408 RapidAir image analysis system sorts out all chords shorter than 6 μm , as they are considered noise.

409

3.3 Combining results from concrete and paste experiments

The results shown in figure 5 can be used to correct the air void analyses that were performed for the concrete samples. For each mixture, steps 1-4 are performed:

1. Calculate the volumetric fly ash content
2. Given the volumetric fly ash content and the linear traverse length in the original air void analysis, calculate the expected number of chords generated due to cenospheres in each chord size interval.
3. Subtract the expected number of chords due to cenospheres from the number of chords in each chord size interval registered in the original air void analysis. The result is a corrected chord table.
4. Use the corrected chord table to calculate the total air content and specific surface area of air voids; these figures can then be used to calculate the spacing factor.

Table 5 shows results from the original and the corrected air void analyses, respectively:

Table 5: Results from the original air void analysis and results after the chord table has been corrected to take the presence of voids generated by cenospheres into account.

Mixture ID	Air content in hardened concrete		Specific surface		Spacing factor	
	A_{hard} [%]		S [mm ⁻¹]		L [mm]	
	original	corrected	original	corrected	original	corrected
000	7.33	-	42.2	-	0.081	-
025	6.44	6.32	47.1	44.9	0.080	0.091
033	5.03	4.86	40.8	36.6	0.118	0.135
044	4.31	3.99	44.2	37.6	0.112	0.137
050	4.74	4.34	40.4	33.2	0.119	0.152
050EA	7.57	7.18	44.3	40.2	0.075	0.087

For all air void parameters, the largest correction is made for mixture 050. With regard to total air content, the correction for mixture 050 is 0.40% (percentage point). This is also the largest correction relative to the total air content before the correction (8%). The correction of specific surface is more distinct. For mixture 050, the specific surface is reduced 18% due to the correction. Both the correction of the total air content and the correction of the specific surface has an impact on the calculated spacing factor. All the corrected spacing factors are still below the critical spacing factor of 0.20 mm. However, the difference between a spacing factor of 0.081 mm (mixture 000) and a spacing factor of 0.152 mm (mixture 050) is significant, and they cannot be said to be on the same level within the accuracy of the method.

The effect of cenospheres on the outcome of air void analysis has to the knowledge of the authors not been quantified before. The results from the present study are not directly transferrable to other

studies with high contents of fly ash, where air void analyses have been performed, as the amount of cenospheres in the fly ash and the size distribution of voids generated by the cenospheres are closely related to the fly ash source. However, it is reasonable to assume that also in other studies reported in the scientific literature, the air void analyses may misrepresent the actual air void structure if the concrete contains a high volume of fly ash. For example in [25], where Yıldırım et al. test FA/C ratios that are even higher than in the present study. In their study, mortars with FA/C ratios 1.2, 2.2, and 4.2 are tested This corresponds to FA/(C+FA) ratios 0.55, 0.69, and 0.81. Even though the mixtures are not air entrained, they show spacing factors of 0.129 mm, 0.069 mm, and 0.057 mm, respectively. Likewise, there seems to be a systematic trend, where higher fly ash contents result in lower spacing factors. The water to cementitious material (W/CM) ratio is in all cases 0.27. Despite the low W/CM ratio and the seemingly good air void structure, none of the mixtures passes an accelerated freeze/thaw test.

Figure 6 shows the cumulated scaling after 56 freeze/thaw cycles (also depicted in figure 3), but here as a function of the corrected spacing factor:

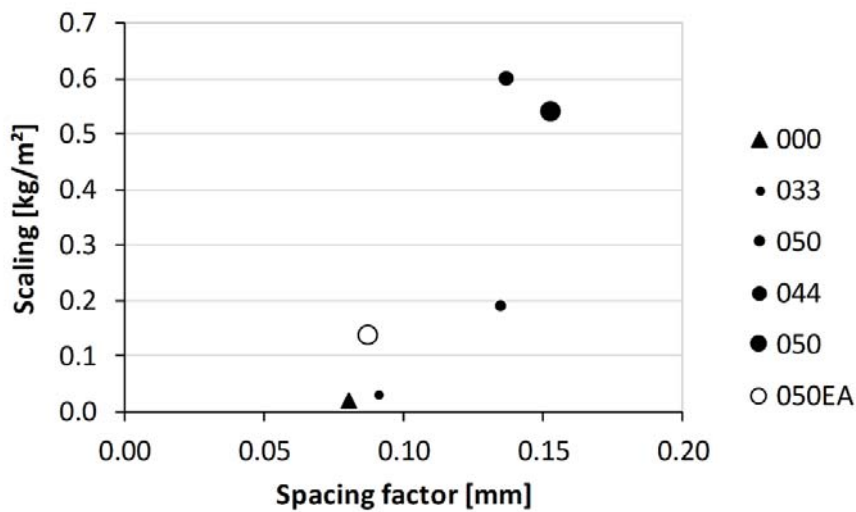


Figure 6: Cumulated scaling after 56 freeze/thaw cycles vs. corrected spacing factor.

Figure 6 shows that although the corrected spacing factor of mixture 050EA is on the same level as the spacing factors of mixtures 000 and 025, the scaling due to frost action is approximately 5 times higher. Figure 6 also shows that for mixtures 044 and 050, the scaling is considered critical, even though the spacing factors are lower than 0.20 mm, which is normally an acceptable spacing factor. It is therefore concluded that the presence of cenospheres only partly can explain why the frost resistance of concrete with high contents of fly ash performed worse in accelerated freeze/thaw tests than anticipated based on information on the concrete composition and results from air void analysis; the presence of cenospheres is not likely to be the full explanation.

Valenza and Scherer state that the inferior salt frost scaling resistance of concrete with high contents of fly ash may be caused by the curing procedure used prior to freeze/thaw testing [26]. In the present study a standardized method is used, where the concrete is sealed the first day after casting, then it is submerged in water for 6 days and finally stored 21 days at 20°C, 65% RH. This procedure may be representative for e.g. an in-situ casting, as drying protection normally is not

maintained for more than a week. However, it is likely that a short moist curing period will lead to a larger strength reduction for concrete with fly ash, compared to concrete with cement as the only binder, because concrete with a high content of fly ash due to slower hydration is more vulnerable to loss of water. The lower strength will again result in inferior salt frost scaling resistance. It may be speculated that the compressive strength measured in the present study is not identical to the strength of the specimens that were subjected to accelerated freeze/thaw testing, because the curing procedures of the two standardized test methods were not alike (see sections 2.5 and 2.7). Data from literature may indicate the magnitude of the difference. Ramezaniapour and Malhotra measured compressive strength development for concrete cured at various conditions [27]. For concrete with cement as only binder, the 28 days compressive strength of concrete moist cured 2 days after demoulding and then left in the laboratory (23°C, RH not specified) was 95% of the compressive strength of concrete that had been moist cured all the time between demoulding and testing. For concrete where low calcium fly ash constituted 58% of the binder, the compressive strength for concrete moist cured 2 days after demoulding was only 86% of the strength registered for concrete that was fully moist cured. In another study [28] with similar binder compositions (57% low calcium fly ash in concrete with high contents of fly ash), cast concrete cylinders were either stored in a fog room (23°C, RH>95%) until time of testing, or they were stored 7 days under wet burlap in the laboratory and then air-cured outdoor. Here, the 28 days compressive strength of concrete specimens cured in air is approximately 80% of the strength for moist-cured specimens. However, it also has to be taken into account that the outdoor temperature was lower than the temperature in the fog room. In a recent review [29], results are compared for concrete with fly ash, where the specimens are either moist cured (20°C, in water bath or in fog room) or moist cured for 7 days and then air dried (20°C, 65% RH). The review comprises more than 100 concrete mixtures with low calcium fly ash (up to 50% of the binder content) for each drying condition. The conclusion is that

there is no systematic difference between the two curing conditions. The difference in curing conditions in [29] is similar to the difference in curing conditions for specimens for compressive strength testing and accelerated freeze/thaw testing, respectively in the present study. If strength reduction due to drying should explain the poor salt frost scaling resistance for mixtures 044 and 050, then the strength reduction should be approximately 30% to match the strength of mixture 000. A 30% strength loss does not seem plausible, when the strength reduction is only up to 20% in [27, 28], where the drying condition during air curing is more severe.

The results of the present study indicates that neither the presence of cenospheres nor strength reduction due to drying can explain the susceptibility to salt frost scaling. Therefore, there seems to be at least one other reason why concrete with high contents of fly ash is vulnerable to salt frost scaling.

4. New hypothesis: Combined action of several degradation mechanisms

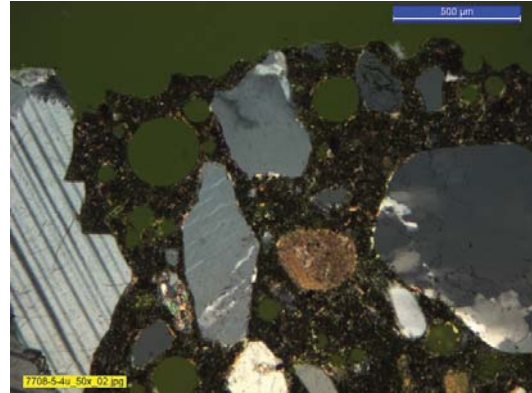
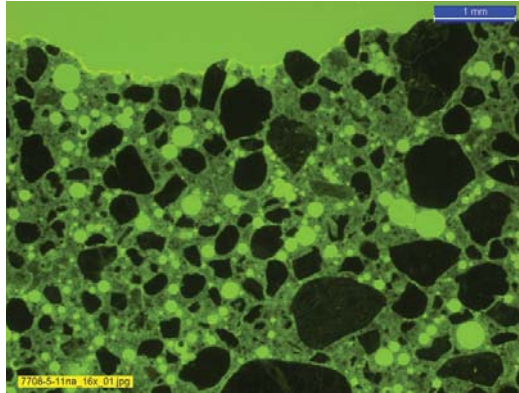
It was decided to conduct a follow-up investigation comprising fluorescent epoxy impregnated thin section analysis and scanning electron microscopy (SEM) of the freeze/thaw exposed test surfaces. Figure 7 shows selected photos of thin sections. Figure 8 shows an example of a SEM photo.

Mixture
ID

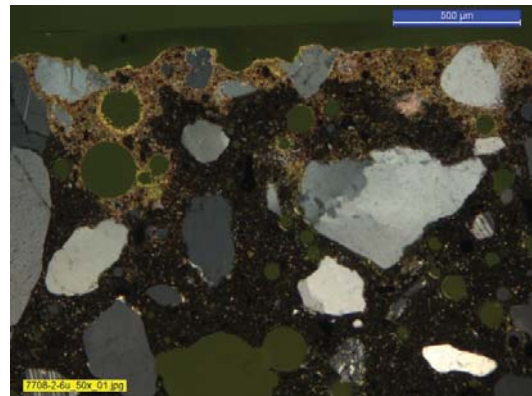
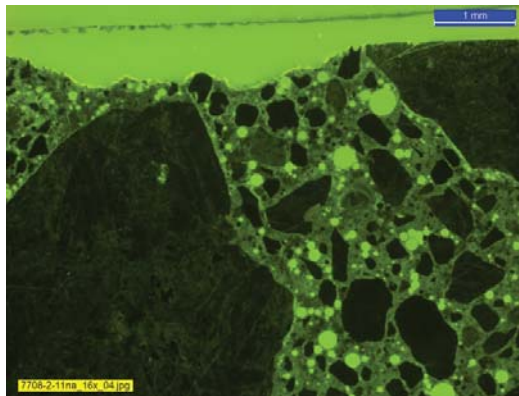
Microscope setting:
Fluorescence light mode
(magnification: blue bar equals 1 mm)

Microscope setting:
Cross polarized light mode
(magnification: blue bar equals 0.5 mm)

000



033



050

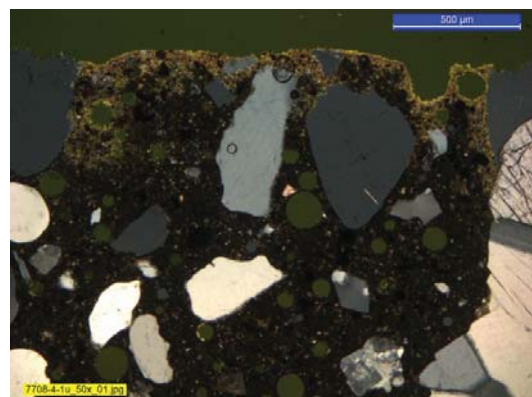
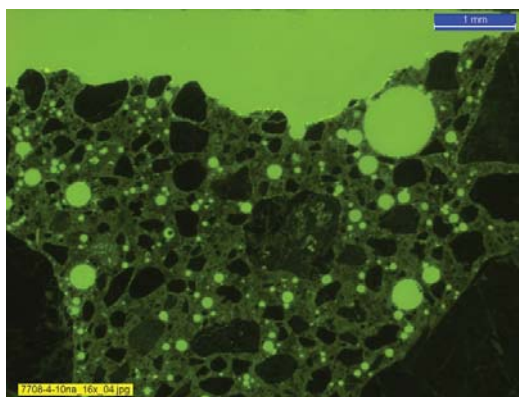
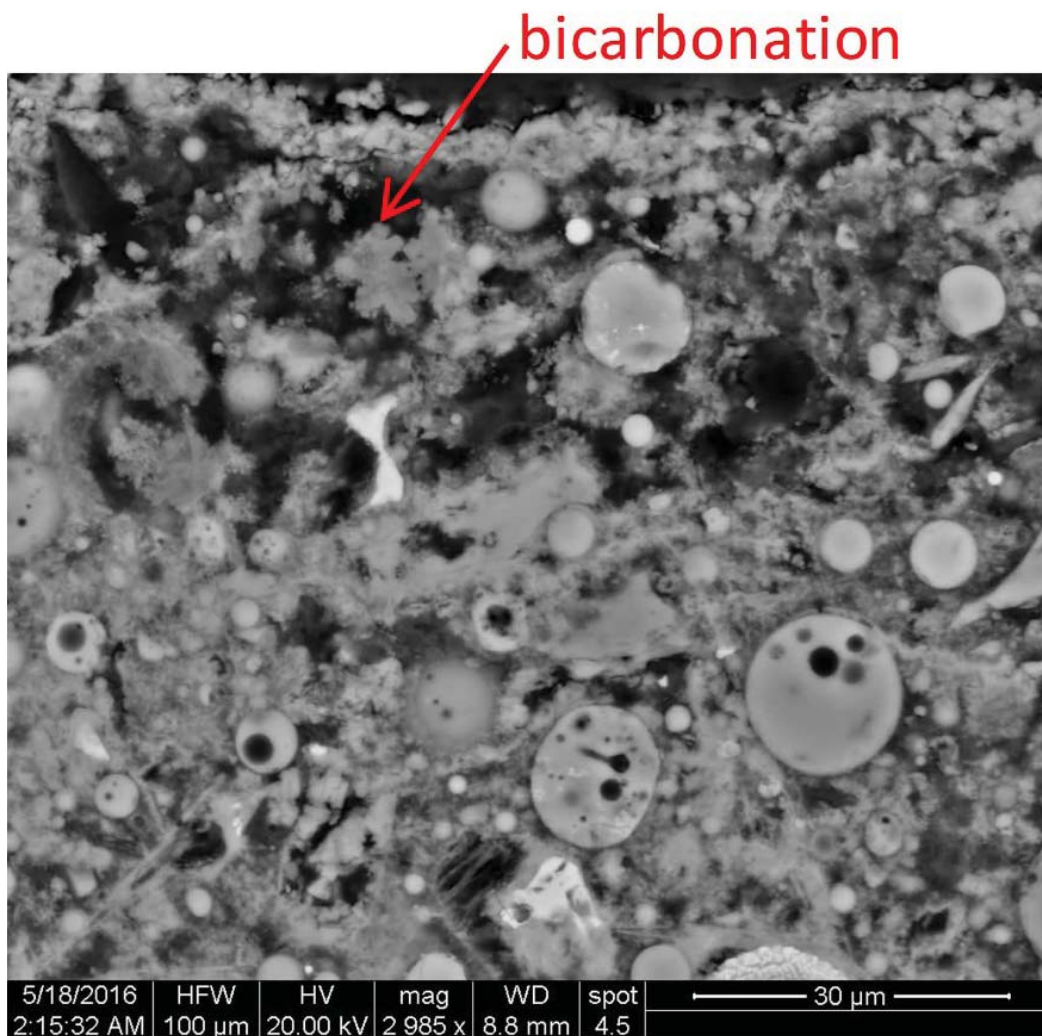


Figure 7: Concrete surfaces after exposure to freezing and thawing.



518 *Figure 8: SEM photo of specimen from mixture 033 after freeze/thaw exposure (magnification: blue*
 519 *bar equals 30 μm).*

520

521 The following observations are made during the examination of the surfaces:

522

- 523 • The thin sections show that all concrete mixtures have systems of fine and well-dispersed air
 524 voids as also shown by the air void analyses.

- After freeze/thaw exposure, the surface roughness increases for specimens that have shown scaling. However, the specimens that have suffered from scaling do not show signs of inner cracking.
- All specimens except the specimen from mixture 000 show a carbonated zone just below the test surface after freeze/thaw exposure. The thickness of the carbonated layer is highest for mixtures 025 and 033, where the extent of the carbonated zone is approximately on the same level.
- SEM photos show bicarbonation (“popcorn calcite”) in the carbonated layer for all samples except mixture 000.

Several things seem unusual. For example, no signs of inner cracking are seen in the concrete that at the same time shows severe scaling during the salt frost scaling test. For concrete in general, there will normally be fine cracks in the zone just below the scaled surface [30]. However, our observation of salt frost scaling without inner cracking is not without precedent for concrete with high contents of fly ash. Bilodeau et al [31] made a study comprising 2 types of cement and 8 different types of fly ash (16 mixture combinations). In all mixtures, fly ash made up 63% of the powder by mass, $W/(C+FA)=0.33$, and all mixtures were air entrained (spacing factors in the range 0.11-0.21 mm). All mixtures were tested both according to ASTM C 666 procedure A (freezing and thawing in pure water) and according to ASTM C 672 (salt frost scaling test). In the ASTM C 666 test, 13 of 16 mixtures showed durability factors surpassing 100 after 1000 freeze/thaw cycles, and all mixtures passed the test. Thus, there was no indication of the high volume fly ash mixtures having problems with inner cracking. However, all mixtures showed levels of salt frost scaling during the ASTM C 672 test that were not satisfactory; all mixtures except one received the visual

548 rating 5 (severe scaling) already after 50 freeze/thaw cycles, and the last mixture was rated 4
549 (moderate to severe scaling).

550

551 In the present study, it is also surprising that carbonation has developed in the surface layer of most
552 specimens during freeze/thaw exposure. During testing, the specimens were covered by 3 mm of
553 NaCl solution, and the solution was again covered with a plastic sheet to prevent evaporation, so the
554 exposure to CO₂ from atmospheric air in the freezing chamber was very limited. The freeze/thaw
555 test was performed for 3 specimens for each mixture. Originally, 4 specimens were prepared for
556 testing, but the fourth specimen was never placed in the freezing chamber. Therefore, it was
557 possible to make thin sections from these extra specimens, which had followed the test scheme until
558 31 days after casting, including 3 days of capillary suction with de-ionised water. These thin
559 sections did not show signs of carbonation, confirming that the carbonation had taken place during
560 the period of freeze/thaw exposure.

561

562 Even though the highest carbonation depth is observed for mixtures 025 and 033, it is not evident
563 that carbonation happens faster for these mixtures than for mixtures 044 and 050, as carbonation
564 depth is measured relative to the surface after scaling has been removed. In fact, it could well be
565 that carbonation has progressed further in mixtures 044 and 050 than in mixtures 025 and 033, but
566 for mixtures 044 and 050 part of the carbonated layer has been removed due to scaling.

567

568 It is therefore suggested that for concrete mixtures with high contents of fly ash, surface scaling is
569 due to combined action of chemical degradation and frost action. Bicarbonation appears in concrete
570 with a low content of calcium hydroxide [31]. Where regular carbonation may lead to a
571 densification of the concrete and thereby slow down transport of matter in the surface layer [33],

bicarbonation reduces concrete strength and makes the concrete more permeable [31]. If a chemical reaction takes place in the surface layer and thereby locally reduces the concrete quality, the surface layer is going to scale off during the following freeze/thaw cycle. The development of scaling shown in figure 3 also supports this explanation. Here, for mixtures 033 and 044, the rate of scaling seems to accelerate during periods, where the freezing chamber accidentally shut off. This may be because there was longer time for the chemical degradation to develop between freeze/thaw cycles.

Two types of chemical surface degradation were briefly investigated by conducting salt frost scaling tests for mixture 050EA in parallel to the standardized procedure described in section 2.7:

- a. Leaching
- b. Chemical reaction with de-icing salt

a. Leaching (hydrolysis of the hardened paste)

Calcium hydroxide has a relatively high solubility in water, compared to other hydration reaction products. If the concrete is in contact with water, calcium hydroxide can be leached out. When the calcium hydroxide is eliminated, other parts of the hardened cement paste will also start to decompose [34]. In concrete with high contents of fly ash, the amount of calcium hydroxide in the hardened cement paste is low. There are two reasons for this. First, less calcium hydroxide is formed during cement hydration, because there is less cement from the beginning. Second, calcium hydroxide formed during cement hydration is used during the pozzolanic reaction of the fly ash. Therefore, in mixtures with high contents of fly ash less calcium hydroxide needs to be leached out before other parts of the hardened cement paste starts to decompose, and therefore concrete with high contents of fly ash may be more vulnerable to hydrolysis of the paste.

596

597 Rosenqvist [35] investigated the combined effect of leaching and frost action. In his experiments, he
598 studied the degradation occurring from leaching alone (without frost action) and the degradation
599 occurring during freezing and thawing (without leaching) as well as the degradation developing
600 during alternating leaching and frost action. His experimental results show that the combination of
601 leaching and freezing and thawing leads to more severe surface damage than the sum of damage
602 developed when one damage mechanism works at a time. This synergistic effect explains why
603 hydraulic structures in soft river water suffers from surface scaling, though concrete exposed to
604 freeze/thaw testing with pure water in the laboratory normally shows none or very limited scaling.
605 The difference is that the real structure is subject to leaching during summer, and then the degraded
606 surface layer scales off during the freeze/thaw cycles during winter. This does not happen in the
607 freeze/thaw test in the laboratory, where the solution in contact with the concrete surface is stagnant
608 (not flowing), and where there is shorter time for leaching to develop.

609

610 To investigate the combined action of leaching and freeze/thaw action, a freeze/thaw test was
611 conducted for mixture 050EA as described in section 2.7, but where the NaCl solution was changed
612 after every frost period (i.e. every 24 h) to intensify leaching. The experiment was stopped after 14
613 freeze/thaw cycles. There was no difference in scaling compared to the standard procedure, where
614 the freezing medium was changed after every 7 cycles.

615

616 *b. Chemical reaction with deicing salt*

617 If the surface is weakened by a chemical reaction with the deicing salt, then it is expected that the
618 degree of damage changes, if the deicing salt used in the standardized method is replace by another
619 deicing salt.

620

621 A freeze/thaw test as described in section 2.7 was carried out, but using CaCl_2 solution instead of
622 NaCl solution. The concentration of the CaCl_2 solution was adjusted, so the ion concentration was
623 identical to the 3% NaCl solution, so the freezing points of the two solutions were similar. After 56
624 freeze/thaw cycles, the amount of scaling for the test with CaCl_2 was 150% higher than the scaling
625 registered when using NaCl.

626

627 Based on this very preliminary study, it seems like the increased salt frost scaling observed for
628 concrete with a high content of fly ash is not due to combined action of leaching and
629 freezing/thawing. It may be due to a chemical reaction where chloride takes part, as the chloride
630 concentration in the CaCl_2 solution is higher than in the NaCl solution ($\text{Ca}:\text{Cl} = 1:2$; $\text{Na}:\text{Cl} = 1:1$).

631

632 Balonis et al. have described how chloride ingress changes the mineralogy of hardened cement
633 paste [36]. Their thermodynamic modelling is based on 25°C , not freezing temperatures, but it may
634 still be of relevance. In case of a binder based on pure Portland cement and a sufficiently high
635 chloride concentration, chloride will substitute sulfate in monosulfoaluminate ($\text{SO}_4\text{-AFm}$) and form
636 Freidel's salt (Cl-AFm). The liberated sulfate ions will react with more monosulfoaluminate and
637 calcium hydroxide to form ettringite (AFt). Seen in isolation, the transformation of $\text{SO}_4\text{-AFm}$ to
638 Cl-AFm reduces the volume of solid (calculated by using table values for molar volume in e.g.
639 [37]). However, this is more than compensated by the formation of ettringite, as this is an expansive
640 reaction, so the net effect of the chloride binding is a densification of the surface exposed to
641 chloride ingress. In the present study, the first exposure to chloride takes place 31 days after casting.
642 At this age, the amount of calcium hydroxide in the hardened cement paste is much lower for
643 mixtures containing fly ash than for the mixture without fly ash [38] (and also explained for

leaching). Due to the low content of calcium hydroxide in mixtures with fly ash, it is likely that the transformation from $\text{SO}_4\text{-AFm}$ to Cl-AFm only to a very limited extent is followed by ettringite formation, so in these cases the chloride binding will make the surface layer more porous. Balonis et al. [36] have also described the change of phase distribution due to chloride exposure, if lime stone filler is present in the binder. Here the carbonate during hydration is bound in monocarboaluminate ($\text{CO}_3\text{-AFm}$). This AFm phase can also take part in ion exchange, so Cl-AFm is formed during chloride ingress. The liberated carbonate will form calcite. CEM I cement is used in the present study, so minimum 95% of the cement is clinker. However, the cement probably also includes small amounts of limestone filler. Therefore, the carbonated layer as well as popcorn calcite may have formed during the time of chloride exposure, and the carbonate originates from the cement, not from atmospheric air. Both carbonation and popcorn calcite is also seen in samples taken from marine structures below the average water level [39]. As such, the presence of popcorn calcite is a sign of the change in mineralogy in the surface layer due to chloride ingress, and the popcorn calcite is more likely to form in concrete with high contents of fly ash, because here the concrete's content of calcium hydroxide is low. However, the presence of popcorn calcite may be more than just a sign of chemical reaction. It may also be part of the problem with low salt frost scaling resistance, as it increases the permeability of the surface layer [31].

The problem field of combined action that involves both chemical degradation and frost action calls for more research. The classical frost attack is by nature a physical attack associated with the transformation of liquid water to solid ice. If the frost attack is combined with a chemical attack, it is necessary to understand the interplay with the paste matrix and how this interplay is influenced by e.g. binder composition (more than just the physical strength of the paste). Suraneni et al. [40] studied the formation of calcium oxychloride in concrete. It is an expansive reaction that involves

both calcium chloride, CaCl_2 , and calcium hydroxide, $\text{Ca}(\text{OH})_2$, as reactants. As CaCl_2 is often used as de-icing chemical and as the calcium oxychloride formation is favored at low temperatures, the chemical attack aggravates the salt frost scaling. Suraneni et al. [40] demonstrated that the use of fly ash limits calcium oxychloride formation, because the pozzolanic reaction consumes the calcium hydroxide formed during cement hydration, and then calcium hydroxide becomes in short supply for the calcium oxychloride formation. However, the degree of cement substitution needs to be high to effectively bring down the content of calcium hydroxide. Suraneni et al. have suggest 35% cement substitution by fly ash, and even higher substitution levels may be necessary, depending on the fly ash quality [41]. Suraneni et al. warn that the influence of high replacement levels on e.g. salt frost scaling resistance needs to be investigated, before implementing high contents of fly ash as a solution to the problem of calcium oxychloride formation. If the indications we have seen in our laboratory are correct, this solution may cause other problems related to frost resistance.

5. Conclusion

This study demonstrates that when performing air void analysis on samples of hardened concrete, e.g. according to the procedures described in ASTM C 457 and EN 480-11, then hollow fly ash particles will show up as air voids. As the hollows in the fly ash particles are small, they do only to a limited extent add to the registered total air content, but the presence of the hollow fly ash particles may significantly change the measured spacing factor. The magnitude of the error obviously depends on the amount of fly ash in the concrete mixture (as well as on the fly ash quality). In the present study, air entrained concrete mixtures with $\text{FA}/(\text{C}+\text{FA})$ up to 50% were tested. For the mixture with the highest fly ash content, the spacing factor was increased approximately 25% when corrected for the presence of hollow fly ash particles.

The concrete mixtures have also been subjected to accelerated salt frost scaling testing. The concrete mixtures all had comparable compressive strength and comparable air void characteristics, when the correction for hollow fly ash particles had not been applied. For all concrete mixtures except one, mixtures with higher contents of fly ash showed higher amounts of salt frost scaling (a mixture with maximum dosage of fly ash and extra air entraining agent being the exception). The difference in frost resistance between concrete with and without fly ash cannot be fully explained by the distortion of the air void analyses due to the presence of hollow fly ash particles. The corrected air void analyses point to that the critical spacing factor for mixtures with high contents of fly ash is lower than 0.20 mm.

Though it was not part of the experimental plan to investigate the frost damage mechanism itself, the experimental results indicate that for concrete mixtures with high contents of fly ash, there is a combined effect of a chemical surface degradation and the physical frost attack.

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During the review process, we received very detailed comments from the reviewer, as well as references to related projects that we were not aware of. The contribution of the reviewer has both

helped to improve the present paper and been a source of inspiration for our future research related to the frost resistance of concrete with high contents of fly ash. This effort is greatly acknowledged.

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